

Size-Monodisperse Metal Nanoparticles Via Hydrogen-Free Spray Pyrolysis**

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Metal nanoparticles are of interest for a variety of applications because of their unique chemical, electronic, and optical properties. These applications include catalysis,^[1-3] templates for assembly of nanostructures,^[4] conductive pastes for electromagnetic shielding of packaging materials,^[5,6] and size standards for calibration of optical scattering instruments^[7]. Surface defects such as particulate contaminants and surface roughness, and subsurface defects, are of great concern for quality control of products such as semiconductor devices, magnetic storage media and flat panel displays. As device dimensions shrink, detection plays an increasingly important role in increasing product yield.^[8,9] Most studies of defect detection via optical scattering have focused on the detection of dielectric materials such as polystyrene latex (PSL) spheres^[10-13] because solutions consisting of suspensions of PSL particles with a nearly monodisperse size distribution are commercially available, and because the PSL particles can easily be deposited onto wafers. However, it is unlikely that PSL particles are representative of actual industrial process contaminants. Furthermore, the interaction of light between particles and the silicon substrate is much simpler for dielectric materials than for other materials such as metals. A need exists for methods of producing size-monodisperse particles of other materials, particularly metals, deposited onto wafer surfaces for use as optical scattering standards and for evaluating light scattering theories.

In this communication, we present a novel spray pyrolysis process, based upon the use of a co-solvent, for preparing size-monodisperse pure copper particles from metal salt precursors without the addition of hydrogen or any other reducing gas. We selected copper because of its well-defined optical properties at typical incident wavelengths. It is believed that the co-solvent, a low carbon number alcohol such as ethanol or methanol, acts as a reducing agent for the reactive metal particles during the high temperature pyrolysis step. Using this co-solvent approach, size-monodisperse pure copper nanoparticles were prepared from copper nitrate as determined using transmission electron microscope (TEM) images and x-ray diffraction (XRD) and compared to particles formed without an ethanol co-solvent as well as to particles formed from copper acetate.

Spray pyrolysis has been widely used to produce micro and nanoscale metal powders because of its convenient process characteristics compared to gas condensation methods such as plasma reactors and laser ablation.^[14] In a typical spray pyrolysis process, an aqueous solution of precursors is atomized and the stream consisting of droplets suspended in a carrier gas is passed through a tubular furnace. In the furnace, the precursor reacts in the solid phase, forming the final

product powder. After electrostatic classification using a differential mobility analyzer (DMA), the size-monodisperse particles can be deposited onto substrate surfaces using a low-pressure impactor or an electrostatic precipitator. However, preparation of size-monodisperse pure metal particles with well-defined optical constants via spray pyrolysis is challenging because of metal oxide formation. Even if no oxygen is supplied to the reactor, the precursor compound may serve as a source of oxygen. Recently, copper metal particles have been produced using hydrogen to reduce metal oxide particles formed by spray pyrolysis of metal salt precursors.^[15,16] In these processes, though, the concentration of hydrogen required to reduce the metal oxide particles is greater than the flammability limit of hydrogen in air, resulting in a potential safety hazard.

The particle generation and classification system is shown in Figure 1. In our spray pyrolysis process, an atomizer (RETEC^[17]) is used to generate aerosol droplets of precursor solution with a delivery rate of 0.006 cm³/s (20 mL/hr) and a nitrogen carrier gas flow rate of 83 cm³/s (5.0 L/min). Details of the precursor solution preparation procedure are given at the end of this communication. The suspension of precursor droplets in nitrogen is passed first through a diffusion drier, which consists of a screen tube containing the aerosol stream surrounded by silica gel desiccant. The aerosol then passes through a quartz tube heated externally by two horizontal furnaces in series (Lindberg,^[17] type 55035) forming metal nanoparticles by solvent evaporation and precursor decomposition. The furnace temperature for these experiments was 600 °C. Finally, polydisperse metal particles were classified by passing the stream through a bipolar charger (radioactive Kr-85) to obtain particles with a Boltzmann charge distribution,^[18] and a differential mobility analyzer (DMA, TSI, Inc.,^[17] Model 3071), resulting in uniform sized particles. The DMA consists of an inner cylinder rod connected to a DC power supply and an outer tube connected to ground. The charged aerosol enters through an axisymmetric opening along outer cylinder while clean sheath air flows through the axial region. The charged spheres move radially towards the center rod under the influence of the electric field. Near the bottom of the classifying region, a fraction of the airflow consisting of size classified aerosol exits through a slit in the center rod and flows to an optical particle counter or a particle precipitator.^[18,19] In the experiments reported here, the sheath air and outlet flow rates were 167 cm³/s (10 L/min) and 16.7 cm³/s (1 L/min) respectively.

The x-ray diffraction (XRD) patterns of copper particles prepared at 600 °C from 10 % volume fraction of ethanol in water (a), and pure aqueous (b) solutions are shown in Figure 2. For the case of pure water, not only the peaks indicating (111) planes at $2\theta(^{\circ}) = 36.4$ and (200) planes at $2\theta(^{\circ}) = 42.34$ of cuprite were visible, but also a small amount of tenorite phase was present. However, there were no detectable amounts of cuprite phase if the precursor solution contained 10 % volume fraction of ethanol. We attribute our findings to the strong reducing conditions likely resulting from reaction of the co-solvent within pores or at the surfaces of the metal particles at high temperatures. In the previously reported studies of copper particle formation,^[15,16] pure copper particles could be produced using a mixture of 7-volume percent hydrogen gas in nitrogen in the pyrolysis reactor. In those cases, hydrogen gas played a significant role, reducing the oxide products that result from the oxygen impurities and by-products into pure metals. Here, we demonstrate that use of a co-solvent as a reducing agent accomplishes the same role under safer conditions.

The particles, after passing through the bipolar charger, are either neutral, singly, or multiply charged according to the Boltzmann distribution.^[18] Unfortunately, larger multiply charged particles can be classified with smaller singly charged particles by the DMA. Figure 3 shows the size distribution of particles produced at 600 °C from copper nitrate 0.30 mol/L solution

containing 10 % volume fraction of ethanol measured using the DMA coupled with a condensation nucleus counter (CNC, TSI, Inc., ^[17] model 3022A). Size classification of charged particles is affected by the particle size distribution because the fraction of charged particles depends on particle size (for example, according to the Boltzmann distribution, a sample of 100 nm particles would contain 42% neutral, 48 % singly charged, 9 % doubly charged, and 1 % triple charged particles) ^[18]. Considering this size dependency, along with the particle size distribution of the particles in our system, as shown in Figure 3, a sample classified using DMA to select 113 nm particles will contain approximately 4% by number of doubly charged 226 nm particles and less than a percent of triply charged 339 nm particles (we cannot measure the number concentration of particles greater than 300 nm using the DMA with the sheath and aerosol flow rates given previously).

Our solution to this multiple charging problem, as shown in Figure 1, is to use a droplet impactor plate with four 0.5 mm holes to remove most of droplets in the atomization step that would otherwise evaporate and react to form particles greater than 160 nm. As shown in the figure 3, the possibility of collecting multiply charged larger particles together with smaller particles of the desired size is effectively eliminated. TEM images of copper particles formed at 600 °C using the DMA to select 100 nm particles in size are shown in Figure 4. The number mean diameter of particles classified to be 100 nm by the DMA was found to be 101 nm with standard deviation of 3 nm by analysis of the TEM images. The particles are very uniform with respect to size (geometric standard deviation of 1.03), and spherical in shape, ideal for use as standard materials for light scattering studies, especially for testing scattering models. By changing the concentration of metal salt in the precursor solution and by adjusting the voltage applied to the DMA, a range of size-monodisperse samples can be produced. Several samples of uniformly sized copper particles have been used to test the validation of light scattering models. ^[7]

In conclusion, pure copper nanoparticles were produced using a co-solvent approach avoiding the use of hydrogen or other reducing gases. Compared with the particles formed without the co-solvent, the addition of alcohol has a significant effect on preventing oxidation, which is attributed to the strong reducing atmosphere created during co-solvent decomposition. Furthermore, we could classify uniform size particles by using a droplet impactor plate to eliminate larger droplets at the atomizer prior to entering the reactor furnace. These size-monodisperse particles can be deposited on a silicon substrate to obtain a specific particle number density by controlling deposition parameters, and they can further be used as a particle standard for testing light scattering models for semiconductor metrology.

Experimental

Solution preparation: All chemicals are reagent grade (Aldrich ^[17]) and were used without further purification. The concentration of the copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}]$ precursor solution was 0.30 mol/L. Nanopure deionized water (resistivity $\rho > 18.0 \text{ M}\Omega$) was used for all solutions. The 10 % volume fraction of ethanol solution was made prior to adding metal precursors to the solution. All solutions were stirred for 3 hours using a magnetic stirrer.

Characterization: For the x-ray diffraction spectra, particles were collected by filtration immediately downstream of the furnace. The x-ray diffraction of the film was carried out using a Philips ^[17] PW 1800 diffractometer with a graphite monochromator and $\text{CuK}\alpha$ radiation.

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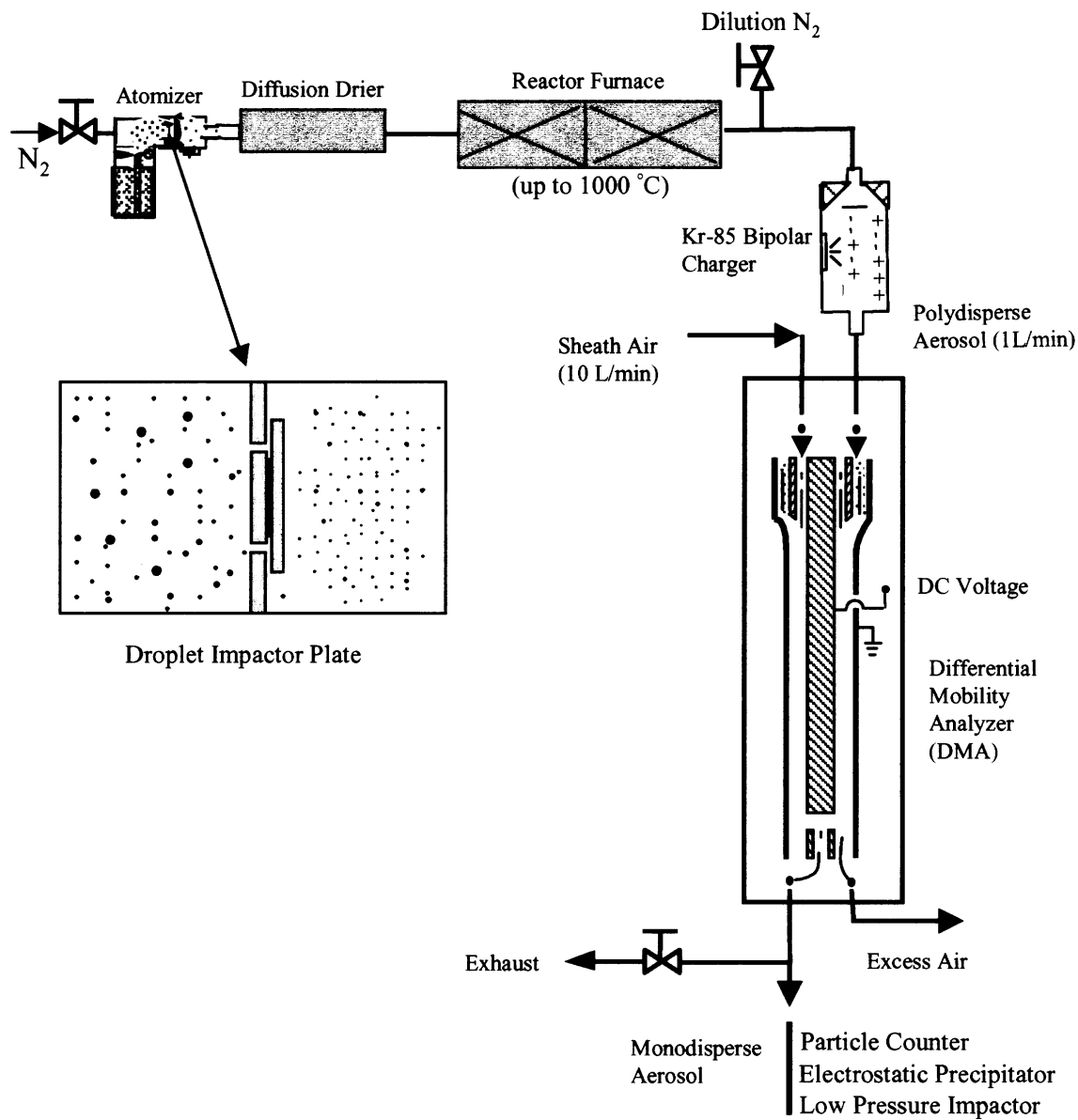


Fig. 1. Spray pyrolysis system for particle generation and classification.

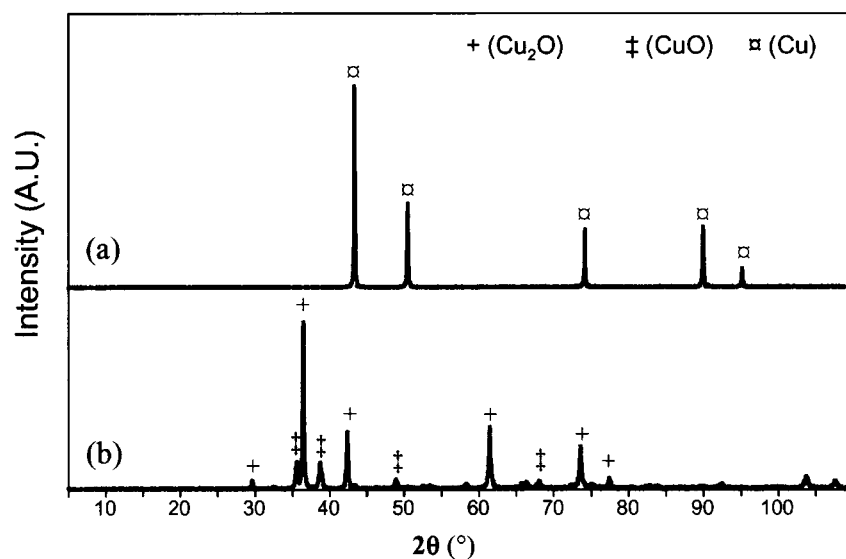


Fig. 2. X-ray diffraction (XRD) patterns of copper particles prepared at 600 °C from 0.30 mol/L copper nitrate in (a) 10 % volume fraction of ethanol and (b) pure aqueous solutions.

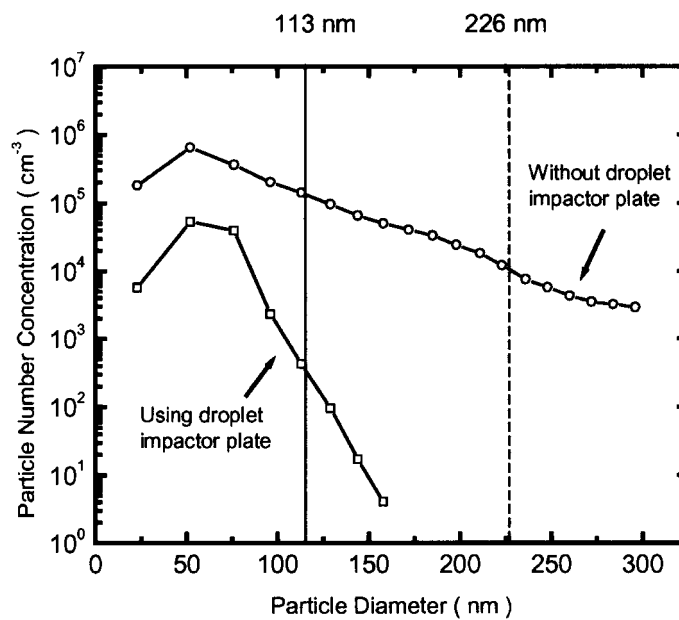


Fig. 3. Typical particle counts for the size classification of particles formed at 600 °C, obtained using the condensation nucleus counter. The droplet impactor plate with four 0.5 mm holes was used after the atomizer before the diffusion drier to remove big droplets that would otherwise react to form multiply charged particles.

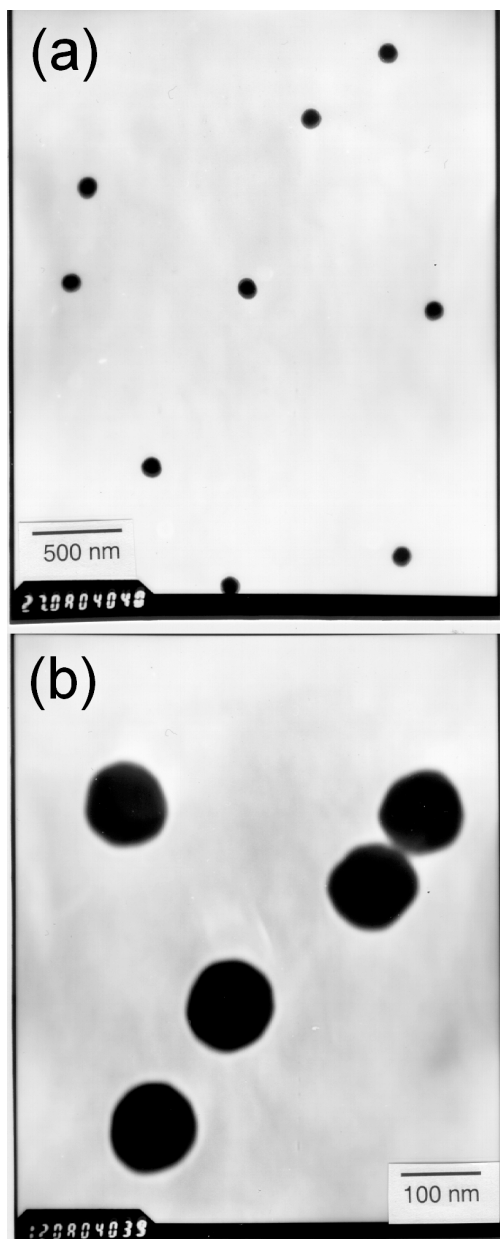


Fig. 4. TEM images of copper particles produced at 600 °C. Particles were classified using the differential mobility to select particles 100 nm in diameter: (a) 27,000 magnification, (b) 120,000 magnification.